PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-116218
(43)Date of publication of application : 27.04.1999

(51)Int.Cl. C01B 31/02

(21)Application number : 09-285360
(22)Date of filing : 17.10.1997

(71)Applicant : OSAKA GAS CO LTD
(72)Inventor : YAMAGUCHI CHIHARU
MATSUMURA YUJI
MATSUI FUMIO

(54) PRODUCTION OF SINGLE LAYERED NANOTUBE

(57)Abstract:
PROBLEM TO BE SOLVED: To produce single layered nanotubes relatively uniform in diameter and length in a high yield.
SOLUTION: When carbon nanotubes are produced by a dry process such as laser beam vapor deposition, resistance heating, arc discharge, high-frequency induction heating, a plasma process, thermo-CVD, electron beam vapor deposition or combustion, starting material used is (1) highly metal dispersed carbon, that is, carbon contg. dispersed metal particles of ≤100 nm particle size, e.g. metal dispersed carbon obtd. by adding starting material for the metal to starting material for carbon and carrying out liq. phase reaction and carbonization, metal plated carbon, metal intercalated or doped carbon or a metal-carbon composite material obtd. by mechanical alloying, (2) metal combined carbon particles, that is, metal-carbon combined particles of ≤100 nm particle size, e.g. metal-carbon combined particles obtd. by feeding starting material for carbon such as methane and starting material for the metal such as an organometallic compd. into plasma or (3) methane and a metal or its compd.

LEGAL STATUS
[Date of request for examination]
[Date of sending the examiner's decision of rejection]
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
[Date of final disposal for application]
[Patent number]
[Date of registration]
[Number of appeal against examiner's decision of rejection]
[Date of requesting appeal against examiner's decision of rejection]
[Date of extinction of right]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention offers the method and the raw material for manufacture for manufacturing in detail the monolayer nanotube with which **** and Itonaga gathered comparatively by high yield about the manufacture method of a carbon nanotube, and the raw material for manufacture.
[0002]
[Description of the Prior Art] A carbon nanotube is carbon of the shape of a tube which has the structure which the graphite (graphite) sheet closed in the shape of a cylinder. There are a multilayer nanotube which has the multilayer structure which the graphite sheet closed in the shape of a cylinder, and a monolayer nanotube which has the monolayer structure which the graphite sheet closed in the shape of a cylinder in a carbon nanotube. The multilayer nanotube was discovered by Iijima in 1991. That is, it was discovered that a multilayer nanotube exists in the lump of the carbon deposited on the cathode of an arc discharge method. Then, research of a multilayer nanotube was made positively, and by the time the multilayer nanotube was so much compoundable in recent years, it became.
[0003] Composition of a monolayer nanotube was simultaneously reported by the group of Iijima and IBM in 1993. The electronic state of a monolayer nanotube is predicted theoretically and it is thought that electronic physical properties change with how to roll Larsen from a metal-property to a semiconductor-property. Therefore, promising ** of the monolayer nanotube is carried out as an electronic material of the future. As a use of others of a monolayer nanotube, nano electronics material, a field-electron-emission emitter, the high directivity radiation source, the source of a soft X ray, single dimension conduction material, high temperature conduction material, hydrogen storage material, etc. can be considered. Moreover, it is considered by surface functionalization, metallic coating, and the nature endocyst of a foreign matter for the use of a monolayer nanotube to spread further.
[0004] Conventionally, a monolayer nanotube mixes metals, such as iron, cobalt, nickel, and a lanthanum, in the carbon rod of an anode plate, and is manufactured by performing arc discharge. However, it was difficult to manufacture the monolayer nanotube with which a multilayer nanotube besides a monolayer nanotube, a graphite, and amorphous carbon are intermingled, yield is low, and also **** and Itonaga of a monolayer nanotube have variation, and **** and Itonaga gathered comparatively in the product by this method by high yield. Therefore, in the present condition, it has been a big technical problem to manufacture the monolayer nanotube with which **** and Itonaga gathered comparatively by high yield.
[0005]
[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the manufacture method of the carbon nanotube for manufacturing the monolayer nanotube with which **** and Itonaga gathered comparatively by high yield, and the raw material for manufacture for it.
[0006]
[Means for Solving the Problem] As a result of repeating research wholeheartedly, the graphite sheet of a nanotube It grows up considering an about several microns metal as a nucleus from several nm, By growing up the metal whose grain size is nano order (100nm or less) about that big growth of a graphite sheet, and **** and Itonaga of a nanotube are influenced with the particle size of the metal used as a nucleus, and a graphite sheet as a nucleus It became clear that the monolayer nanotube with which **** and Itonaga gathered comparatively generates by high yield. Then, this invention persons considered using the carbon which distributed the metal to nano order as a raw material, and completed this invention.
[0007] this invention -- a dry process (for example, a laser vacuum deposition, a resistance heating method, an arc discharge method, a radio frequency heating method, the plasma method, heat CVD, an electron ray vacuum deposition, and a combustion method -- preferably) Circulating inert gas to along the dry process carried out in a vacuum or inert gas or hydrogen gas, for example, the wall of a container In the method of manufacturing a carbon nanotube by the dry process carried out in inert gas or hydrogen gas The metal particles whose grain size is 100nm or less about the graphite sheet which forms a nanotube are used as a nucleus. :(1) metal quantity distribution carbon which is in the manufacture method of the monolayer nanotube characterized by using one sort chosen from the group which consists of the following (1) - (3), or two sorts or more as making it grow up or a raw material, That is, grain size is 100nm or less (10nm or less still more preferably 50nm or less preferably). To the carbon which the metal particles which are 1nm or more distributed, for example, a carbon raw material, usually, a metal raw material The metal distribution carbon which added (for example, the organometallic

compound) and was carbonized after the solution layer reaction, The carbon which carried out metal plating, the carbon which intercalated or doped the metal, The metal graphite composite material, (2) metal compound carbonizing elementary particle which were composite-ized by the mechanical alloying method, That is, grain size is 100nm or less (10nm or less still more preferably 50nm or less preferably). Usually, the composite-ized particle of the metal and carbon which are 1nm or more, for example, the composite-ized particle of the metal and carbon which are obtained by supplying a carbon raw material (for example, methane) and a metal raw material (for example, organometallic compound) into plasma, (3) methane and a metal, or metallic compounds.

[0008] (1) Metal quantity distribution carbon, i.e., grain size, is 100nm or less (50nm or less preferably). Furthermore, the carbon which 10nm or less of metal particles which are usually 1nm or more distributed preferably, A metal raw material (for example, organometallic compound) is added to a carbon raw material. For example, after a solution layer reaction, The carbonized metal distribution carbon, the carbon which carried out metal plating, the carbon which intercalated or doped the metal, The metal graphite composite material composite-ized by the mechanical alloying method, or (2) metal compound carbonizing elementary particle, That is, grain size is 100nm or less (10nm or less still more preferably 50nm or less preferably). Usually, the composite-ized particle of the metal and carbon which are 1nm or more, for example, a carbon raw material One sort or two sorts or more of raw materials for carbon nanotube manufacture chosen from the group which consists of a composite-ized particle of the metal and carbon which are obtained by supplying (for example, methane) and a metal raw material (for example, organometallic compound) into plasma.

[0009] A metal (preferably Sn, germanium, Pb) useful as a graphitization catalyst as the above-mentioned metal, for example, a transition-metals (preferably Fe, Co, nickel, Pd, lanthanum system element);IVB group's metal,; an actinoids system element (preferably Fm) can be mentioned. these metals -- independent -- or it is used as mixture (a 2 yuan system, 3 yuan system, etc.) -- things can be carried out In this invention, without asking the gestalten (crystallinity etc.) except for the case where a definition is given, especially carbon means carbon at large and also contains a graphite besides common carbon. In this invention, grain size means the overall diameter of a particle and the distributed state (grain size) can be observed by the electron probe microanalyzer (measurement).

[0010]

[Embodiments of the Invention]

As a useful dry process, a laser vacuum deposition, a resistance heating method, an arc discharge method, a radio frequency heating method, the plasma method, heat CVD, an electron ray vacuum deposition, a combustion method, etc. are to compound a dry-process carbon nanotube.

[0011] That it is common to the dry process which generates these carbon nanotubes By heating carbon (graphite), a carbon precursor (for example, organic compound), etc. which are a raw material, they carrying out laser radiation, carrying out electron beam irradiation, carrying out arc discharge, or introducing them into a plasma frame A high energy is given by heat, light, the electron, etc. Evaporation, radical-izing, Ionization, the molecule of the gas which was made to carry out low-molecular quantification and had a very activity high energy, It is generating atomic species and generating the carbon material (carbon material of nano scales, such as fullerene, a carbon nanotube, and soot) of various gestalten in the high-energy state or process cooled.

[0012] In those generation reactions, it turns out that a role with big existence of a metal catalyst is played. A monolayer nanotube can be made to generate efficiently by using the metal distribution carbon which added the metal raw material (for example, organometallic compound) to (1) carbon raw material, and was carbonized after the solution layer reaction as a raw material, (2) metal quantity distribution carbon, (3) metal compound carbonizing elementary particle or (4) methane and a metal, or metallic compounds, and growing up the metal particles whose grain size is 100nm or less about the graphite sheet which forms a nanotube as a nucleus.

[0013] The method of generating a typical carbon nanotube is illustrated below.

[0014] A laser vacuum deposition is a method of performing carbonaceous laser vacuum evaporationo in the flow of inert gas, for example, argon gas. In a laser vacuum deposition, a carbon nanotube generates into a cooling portion by irradiating laser from the upstream of the flow of inert gas at a carbon (graphite) target. A monolayer nanotube can be made to generate efficiently by constituting a part or all of a portion that irradiates the laser of a target from metal quantity distribution carbon or a metal compound carbonizing elementary particle.

[0015] A resistance heating method is a method which various kinds of carbon materials containing a carbon nanotube make generate by carrying out energization heating of the graphite rod in inert gas, for example, gaseous helium. A monolayer nanotube can be made to generate efficiently by constituting some or all of a graphite rod that carries out energization heating from metal quantity distribution carbon or a metal compound carbonizing elementary particle.

[0016] An arc discharge method is a method of making various kinds of carbon materials generating, by carrying out arc discharge of both the carbon electrodes in the state where it detached slightly. By the arc discharge method, a carbon nanotube generates on the wall surface of a container etc. A monolayer nanotube can be made to generate efficiently by constituting a part or all of a carbon electrode (especially positive electrode) from metal quantity distribution carbon or a metal compound carbonizing elementary particle.

[0017] A radio frequency heating method is a method of making various kinds of carbon materials containing a carbon nanotube generating, by passing an eddy current to a raw material graphite, and carrying out heating evaporation of this. A monolayer nanotube can be made to generate efficiently by constituting some or all of a raw material graphite from metal

quantity distribution carbon or a metal compound carbonizing elementary particle.
[0018] By the plasma method, a carbon nanotube generates in process in which the plasma-ized carbon component is cooled in a wall surface. by introducing a carbon precursor (for example, organic compound) etc. into the plasma frame generated by RF guidance etc. A monolayer nanotube can be made to generate efficiently by constituting a part or all of a carbon precursor from methane, and introducing into a plasma frame with a metal or metallic compounds.
[0019] Heat CVD is a method of depositing on a substrate the component which introduced the carbon raw material (organic compound) in the reactor, and pyrolyzed it. In heat CVD, in case the pyrolyzed component deposits on a substrate, a carbon nanotube grows. A monolayer nanotube can be made to generate efficiently by constituting some or all of an organic compound from methane, and introducing in a reactor with a metal or metallic compounds.
[0020] The raw material (1) metal quantity distribution carbon metal quantity distribution carbon for manufacture can be manufactured by the method of being the liquid phase, and carbonizing the raw material mixture which added the metal raw material (for example, organometallic compound) to for example, carbon raw materials (a coal tar, petroleum system heavy oil, synthetic resin, etc.), and added the solvent and the acid if needed if needed, after carrying out non-deliquesce, trituration and, after carrying out an air blowing reaction heat-treating or distilling. Metal quantity distribution carbon can be manufactured also by the method of carbonizing in a macromolecule the metal quantity distribution macromolecule which high-distributed the metal coordination or by making it complex-izing if needed after carrying out non-deliquesce, trituration and. Although especially carbonization temperature is not limited, its about 500-3000 degrees C are desirable.
[0021] Metal quantity distribution carbon can manufacture for example, metal plating carbon by the method of depositing a metal on carbon and forming a metal into an ad atom by electrolysis plating, reduction plating, etc. Metal plating carbon can be manufactured by plating a metal on the front face of the carbon fiber of the shape for example, of felt (JP,4-11058,A). The conditions at the time of plating a metal on carbon can be chosen arbitrarily.
[0022] Electrochemically or in chemical reaction for example, after metal quantity distribution carbon makes carbon intercalate or dope a metal or metallic compounds, it can be manufactured by heat, water, or the method of returning electrically if needed. Here, intercalation makes a metal or metallic compounds, and a graphite react, the making [generate]-intercalation compound to which metal or metallic compounds exists between layers of graphite main ** is meant, and a dope mainly means making a metal or metallic compounds exist in a carbonaceous (graphite) front face or openings other than between layers.
[0023] Making carbon intercalate or dope a metal or metallic compounds can be carried out by the well-known method. For example, there is a solution method which oxidizes a metal or metallic compounds in the solution with which the alligation and the graphite which arrange as a method of intercalating a metal or metallic compounds in carbon where a graphite, a metal, or metallic compounds is separated in a container, heat carbon and a metal, or metallic compounds, and heat mixture with the two-bulb method and graphite which make the steam of a metal or metallic compounds react to carbon, a metal, or metallic compounds exist. A metal or metallic compounds is dissolved in alligation, and there are a graphite and a fused salt method made to react in it. There are a chemistry oxidation style which oxidizes a metal or metallic compounds by the oxidizer, and an electrochemistry method which oxidizes a metal or metallic compounds electrochemically by using a graphite as an electrode in a solution method.
[0024] Metal quantity distribution carbon can be manufactured by the method of composite-izing carbon and a metal by the mechanical alloying method (alloying). For example, a ball mill can be used for the charge of an admixture of crystalline carbon material and a metal powder, and carbon and a metal can be composite[the formation of pressurization detailed, and]-ized mixture and by grinding. With the form of desirable operation, the formation of pressurization detailed and composite-ization are performed so that the grain size of the metal particles in the carbon matrix of the composite particle obtained may be set to 100nm or less.
[0025] If carry out suitable amount combination, crystalline carbon material and a metal powder are made intermingled and the end of these mixed powder is pressurized, while detailed mixture will advance and the homogeneity of each particle will increase, functionality is added to the property which each particle has, and the alloy particle which has a higher performance and higher functionality, i.e., a composite particle, generates. If a high-energy ball mill etc. is used and pressurization is especially carried out by the so-called mechanical-alloying processing, each particle will be processed and will become flat [-like], a new field is exposed, and these new fields are forge-welded, it comes to coalesce, this is repeated, detailed-izing and homogenization advance further with collision / compression impulse force, and the composite particle which has the fine structure of nano order generates.
[0026] (2) A metal compound carbonizing elementary-particle metal compound carbonizing elementary particle can be manufactured by the method (the plasma method) of supplying for example, a carbon raw material and a metal raw material into plasma, and making them composite-izing. A hydrocarbon compound, for example, methane, can be used as a carbon raw material. An organometallic compound can be used as a metal raw material.
[0027] (3) A carbon nanotube can be manufactured by supplying a dry process, evaporating it individually, and carbonizing methane and a metal, metallic-compounds methane and a metal, or metallic compounds. The compound which decomposes in a dry process and generates a metal as metallic compounds, for example, an organometallic compound, can be used.
[0028]
[Example]
In one to example 6 coal tar, the organometallic compound (Co acetylacetonato (Co conversion 1.0at%), Y acetylacetonato

(Y conversion 0.3at%)), the quinoline, and the acetic acid were added, the air blowing reaction was performed at 330 degrees C in it for 3 hours, and the metal quantity distribution isotropic pitch with a softening temperature of 280 degrees C was manufactured in it. When this pitch was observed by the electron probe microanalyzer (EPMA), signs that the metal was distributed highly were observed. Then, non-deliquesce was carried out, it carbonized at 500 degrees C (example 1), 1000 degrees C (example 2), 1500 degrees C (example 3), 2000 (example 4) or 2500 degrees C (example 5), or 3000 degrees C (example 6), and metal quantity distribution carbon was compounded.
[0029] Then, the monolayer nanotube was compounded by making a hole in the positive electrode (carbon rod) of arc discharge, inserting metal quantity distribution carbon there and carrying out arc discharge. Atmosphere was set to helium 50Torr as conditions for arc discharge, it was taken to 25V by discharge voltage, and the discharge current was taken as 100A. It was checked that the monolayer nanotube which has the diameter of about 1-2nm to which were comparatively equal had been obtained with about 80 - 90% of yield by transmission-electron-microscope (transverse electromagnetic) observation. The inclination which the yield of a monolayer nanotube increases was suited as carbonization temperature became high.
[0030] The addition of an example 7 - 9Co acetylacetonato (Co conversion (at%)): The monolayer nanotube was compounded like the example 2 except having changed the addition (Y conversion (at%)) of Y acetylacetonato into 0.1:0.3 (example 7), 0.6:2 (example 8), and 0.9:3 (example 9). It was checked that the monolayer nanotube which has the diameter of about 1-2nm to which were comparatively equal had been obtained with about 80 - 90% of yield by transverse-electromagnetic observation. The inclination which the yield of a monolayer nanotube increases was suited as the addition became high.
[0031] The monolayer nanotube was compounded like the example 2 except having changed the kind of ten to example 11 organometallic compound into Co acetylacetonato (Co conversion 1at%)-Sn acetylacetonato (Sn conversion 0.3at%) (example 10) or Co acetylacetonato (Co conversion 1at%)-Y acetylacetonato (Y conversion 0.3at%)-Sn acetylacetonato (Sn conversion 0.3at%) (example 11). It was checked that the monolayer nanotube which has it **** and the diameter of about 1-2nm to which were comparatively equal had been obtained with about 85 - 90% of yield by transverse-electromagnetic observation.
[0032] Example 12 methane and an organometallic compound (Co acetylacetonato (Co conversion 1at%) and Y acetylacetonato (Y conversion 0.3at%) were inserted into plasma, and metal quantity distribution nano particle was manufactured.) When particle was observed by EPMA, signs that the metal was distributed highly were observed. Then, the monolayer nanotube was compounded by making a hole in the positive electrode (carbon rod) of arc discharge, inserting metal quantity distribution nano particle there, and carrying out arc discharge like examples 1-11. It was checked that the monolayer nanotube which has the diameter of about 1nm to which were comparatively equal had been obtained with 90% of yield by transverse-electromagnetic observation.

[Translation done.]